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Removal of lead (II) from aqueous solution by batch adsorption on various inexpensive adsorbents using experimental design

Taylan Salman, Fulya Aydın Temel[1], Gamze Turan*, Yüksel Ardalı

Engineering Faculty, Department of Environmental Engineering, Ondokuz Mayıs University, 55139 Samsun, Turkey,
Tel. +90 362 3121919; Fax: +90 362 4576094; email: tsalman@omu.edu.tr (T. Salman), Tel. +90 454 3101375; email: fulyaa@omu.edu.tr
(F. Aydın Temel), Tel. +90 362 3121919; Fax: +90 362 4576094; emails: gturan@omu.edu.tr (G. Turan), yukselo@omu.edu.tr (Y. Ardalı)

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ABSTRACT

This study focuses on adsorption of lead (II) using various inexpensive adsorbents, such as dried activated sludge, diatomite, and sepiolite, through the batch process. The data were evaluated using three types of isotherm models to determine the design parameters. Additionally, the adsorption kinetics was analyzed using first- and second-order kinetics. The regression coefficient (R^2) quantitatively evaluates the correlation between the experimental data and the predicted responses. The Box–Behnken design of three factors at three levels was used to determine the important parameters affecting the adsorption of lead (II) by different adsorbents and the results showed that pH, initial concentration, and type of adsorbent in these experiments are the important factors. The Freundlich isotherm model fits for all adsorbents, as indicated by the R^2 values of 0.992, 0.997, and 0.997 for Pb^{2+} adsorption onto dried activated sludge, diatomite, and sepiolite at pH 3, respectively. The adsorption capacity was found as 19.85, 25.24, and 33.37 (mg g^{-1}) for dried activated carbon, diatomite, and sepiolite, respectively. The pseudo-second-order model fits the experimental data very well. For kinetic studies, the R^2 values for Pb^{2+} are 0.989, 0.992, and 0.997 for dried activated sludge, diatomite, and sepiolite, respectively. The obtained R^2 values suggest good adjustments to the experimental results since these values indicate that 99.72% of the variability in the response could be explained by the models.

Keywords: Experimental design; Inexpensive adsorbents; Isotherms; Adsorption kinetics

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1. Introduction

Industrial developments in recent years have left their impression on the environmental reservoirs. Many industries, like the metal plating industry, used heavy metals, and thus produced wastewater containing hazardous waste. The removal of Pb^{2+} from industrial wastewater is a major problem due to the difficulty in treating such wastewaters by conventional treatment method. The presence of lead (II) in wastewater is dangerous to environment living. Lead (II) removal attracts the awareness of environmental engineers due to the stringent environmental regulations.

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*Corresponding author.

[1] Present address: Engineering Faculty, Department of Environmental Engineering, Giresun University, TR-28200, Giresun, Turkey, Tel. +90 454 3101375; email: fulya.temel@giresun.edu.tr.

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Many physicochemical methods have been developed for heavy metal removal from aqueous solutions, including chemical coagulation, adsorption, extraction, ion exchange, and membrane separation processes. Among these methods, adsorption is a highly popular one and has been widely practiced in the industrial wastewater treatment processes [1,2]. The application of such processes is often failed because they cannot guarantee to reduce the metal concentration to the limits dictated by regulatory standards; besides, they also produce waste difficult to treat [3–6].

The most respective and widely used adsorbent material in the adsorption processes in activated carbon. Even though it has a high adsorption capacity, surface area, and a microporous structure, it is restricted to use to its relatively high price, high operation costs, and problems with generation for the industrial-scale applications. This led to a search directed to developing the low-cost and locally available adsorbent materials with the maximum adsorption capacity.

Adsorption capacity depends not only on the porous structure of the adsorbent, but also on its chemical structure. Therefore, the determination of surface area and pore size distribution will not be enough to estimate the adsorption capacity of a material. The adsorbents, having the same surface area, will probably exhibit different adsorption behavior due to their different surface structures. This has led some authors to propose alternative models for the adsorption capacity evaluation, based on adsorption from aqueous solutions of cationic and anionic adsorbents [7–9].

In this study, it has been reported that the results obtained on the batch experiments using different adsorbents, such as dried activated carbon, diatomite, and sepiolite, and their ability to remove Pb^{2+} from wastewater. There have been relatively few studies of the adsorption of heavy metals on these materials. The influence of several parameters for adsorption of Pb^{2+}, such as pH, adsorbent dosage, initial concentration, and contact time, were investigated in the batch experiment. The kinetic data was fitted to different models and the isotherm equilibrium data was fitted Langmuir, Freundlich, and Dubinin–Radushkevich isotherm models.

Although the results involving metal removal by natural materials are significant and promising, these results still need to be better understood regarding the properties of adsorbents for optimizing the conditions of the process. The conventional one-factor-at-a-time approach to optimization is time-consuming, nonfeasible, and inept of getting the true optimum condition due to the lack of interactions among the factors. Experimental design is nowadays a widely used statistical tool for process optimization through a relatively smaller number of systematic experiments that can reduce time, cost, and resources. For this purpose, Box–Behnken design was used to evaluate the data.

2. Materials and method

2.1. Materials

Activated sludge biomass was collected from the Bafra municipal biological wastewater treatment system, Samsun, Turkey. Activated sludge was aerated by feeding it a nutrient solution for 10 d. During this period, the amount of mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) determine the concentration of suspended solids and volatile suspended solids in the aeration tank of an activated sludge biological wastewater treatment plant, sludge volume index (SVI) to determine of the physical characteristics of activated sludge solids, and pH was determined after 10 d and found as 3.46 $g\,L^{-1}$, 1.83 $g\,L^{-1}$, 83.64 $mL\ g^{-1}$, and 5.90, respectively. Then, the biomass was heated by adding 5 N NaOH for 15 min to deactivate the biomass and it was sterilized at 121˚C for 30 min using an autoclave. The activated sludge biomass was separated by centrifugation at 2000 rpm for five minutes, washed twice with distilled water, and then dried at 60˚C until its weight is fixed. The dried activated sludge was crushed by grinder and sieved to <0.063 mm for adsorption experiments.

The diatomite and sepiolite were supplied from Çankırı-Çerkeş and Sivrihisar region, Eskişehir, respectively. The compositions were obtained by the X-ray florescence technique, and the chemical analysis

Table 1
The properties of activated sludge (10 d), the physical properties of the diatomite, and the chemical analysis of sepiolite

Dried activated sludge	
MLSS ($g\,L^{-1}$)	3.468
MLVSS ($g\,L^{-1}$)	1.825
SVI ($mL\,g^{-1}$)	83.642
pH	5.9
Diatomite	
Moisture (%)	80
Water absorption (%)	182
Specific gravity ($g\,cm^{-3}$)	1.9
Loose weight ($kg\,m^{-3}$)	220
pH	7.28
Sepiolite	
SiO_2	29.3
Al_2O_3	0.2
K_2O	0.1
MgO	12.4
Fe_2O_3	0.1
CaO	9.1
Loss on ignition	33.5

is given in Table 1. Standard stock solutions of lead (II) were used to prepare the appropriate concentrations from analytical grade $PbNO_3$. The pH of each solution was adjusted to a predetermined value with 1.0 M NaOH or H_2SO_4.

The adsorption of lead (II) on various adsorbents was studied by the batch adsorption technique at room temperature. The experiments were conducted in Erlenmeyer flasks containing various amounts of various adsorbents and 100 mL of metal ion synthetic wastewater having different concentrations and pH. The flasks were agitated at 120 rpm, the mixtures were filtered, and the filtrates were analyzed for lead (II) by means of atomic absorption spectroscopy with air-acetylene (UNICAM 929).

2.2. Adsorption isotherms

The data obtained was modeled using various adsorption isotherms, including Langmuir, Freundlich, and Dubinin–Radushkevich.

The Langmuir adsorption isotherm based on the assumptions that all adsorption sites are equivalent and adsorption in active sites is independent of whether the adjacent sites are occupied or not, is given in Eq. (1):

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e \tag{1}$$

where q_e (mmol g^{-1}) and C_e (mmol L^{-1}) are the amounts adsorbed Pb^{2+} and concentration in equilibrium, respectively. The constant K_L is the Langmuir equilibrium constant, and the K_L/a_L gives the theoretical monolayer saturation capacity. Therefore, a plot of C_e/q_e vs. C_e gives a straight line of slope a_L/K_L and intercepts at the point $1/K_L$.

The Freundlich model can be expressed as Eq. (2):

$$\log Q_e = \frac{1}{n} \log C_e + \log K_F \tag{2}$$

where K_F (mg g^{-1}) and n (L g^{-1}) are the Freundlich adsorption constants, describing the adsorbent capacity and the degree of non-linearity between the solute concentration in the solution and the amount sorbed at equilibrium, respectively. Therefore, a plot of log Q_e vs. log C_e gives a straight line of slope $1/n$ and intercepts at the point log K_F.

The Dubinin–Radushkevich (D–R) model, which does not assume a homogeneous surface or a constant adsorption potential like the Langmuir model, was also used to test the experimental data. The D–R isotherm can be written by Eq. (3):

$$Q_e = Q_m e^{-\beta \varepsilon^2} \tag{3}$$

where β is a coefficient related to the mean free energy of adsorption (mol^2 J^{-2}), Q_m is the maximum adsorption capacity, and ε is the Polanyi potential (J mol^{-1}). A linear form of this expression is expressed as follow Eq. (4):

$$\ln Q_e = \ln X_m - \beta \varepsilon^2 \tag{4}$$

A plot of ln (Q_e) vs. ε^2 was plotted and coefficient β was determined.

2.3. Adsorption kinetics

In order to investigate the mechanism of adsorption, the first- and second-order kinetic models have been used. The first-order rate expression of Lagergren is represented by the following Eq. (5):

$$\frac{dq}{dt} = k_{1,ad}\left(q_{eq} - q\right) \tag{5}$$

where q (mg g^{-1}) is the amount of adsorbed Pb^{2+} on the adsorbent at time t (min) and $k_{1,\mathrm{ad}}$ (min^{-1}) is the rate constant of first-order adsorption. The integrated form of Eq. (5) is the following Eq. (6):

$$\log\left(q_{eq} - q\right) = \log q_{eq} - \frac{k_{1,ad}}{2.303} t \tag{6}$$

A straight line of log(q_eq − q) vs. t would suggest the applicability of this kinetic model. In order to fit Eq. (6) to experimental data, the equilibrium adsorption capacity, q_eq, must be known. In many cases, q_eq is unknown and as adsorption tends to become immeasurably slow, the amount sorbed is still significantly smaller than the equilibrium amount. Moreover, in most cases the first-order equation of Lagergren does not fit well throughout the contact time [10,11].

Various kinetic models have been reported in the literature to describe the adsorption process. Each model has its own limitations and is derived according to certain conditions. However, the simplest way to describe the kinetics of heavy metal removal from an aqueous solution could be represented using a pseudo-second-order equation [10,11]. The second-order kinetic model is expressed as Eq (7):

$$\frac{dq}{dt} = k_{2,ad}\left(q_{eq} - q\right)^2 \tag{7}$$

where $k_{2,\mathrm{ad}}$ (g mg^{-1} min^{-1}) is the rate constant of second-order adsorption. The integrated linear form of Eq. (7) can be written as Eq. (8):

$$\frac{t}{q} = \frac{1}{k_{2,ad}q_{eq}^2} + \frac{1}{q_{eq}}t \tag{8}$$

where q_t is the amount of solute adsorbed on the surface of adsorbent ($\mathrm{mg\,g^{-1}}$) at any time t (min), q_e is the amount of solute adsorbed at equilibrium ($\mathrm{mg\,g^{-1}}$), and k_2 is the rate constant of the pseudo-second-order equation ($\mathrm{g\,mg^{-1}\,min^{-1}}$).

If the second-order kinetics is applicable, the plot of t/q vs. t of Eq. (8) should give a linear relationship and there is no need to know any parameter beforehand. Contrary to the first-order kinetic model, this one predicts the behavior over the whole range of adsorption, and is in agreement with an adsorption mechanism being the rate-controlling step.

3. Results and discussion

3.1. Effect of the adsorbent dosage

The effect of adsorbent dosage on the removal of lead (II) was studied between 1 $\mathrm{g\,L^{-1}}$ and 20 $\mathrm{g\,L^{-1}}$, and the metal ion removed almost remains unchanged after adsorbent dosage of 5 $\mathrm{g\,L^{-1}}$. Increase in adsorption the adsorbent dosage attributed to the availability of a larger surface and more adsorption sites [12]. With an increase in the adsorbent dosage, the metal ion removal increases. For an adsorbent dosage of 5 $\mathrm{g\,L^{-1}}$, the incremental metal ion removal decreased progressively as the surface metal ion concentration and the solution metal ion concentration approaches an equilibrium with each other. For adsorbent dosages higher than 5 $\mathrm{g\,L^{-1}}$, the removal efficiency becomes almost constant for the removal of lead (II) onto the studied adsorbents. For all adsorbents, while the adsorbent dosage was increased, the removal efficiency increased to 2 $\mathrm{g\,L^{-1}}$, and, later, the adsorption removal efficiency has not change. Therefore, 5 $\mathrm{g\,L^{-1}}$ was used in the adsorption experiments.

3.2. Effect of initial metal ion concentration

The removal efficiency of lead (II) by dried activated sludge, diatomite, and sepiolite initially decreased with increasing lead (II) concentration [12]. At low concentrations, lead (II) in the solution would interact with the binding sites, and thus facilitate almost 78% adsorption onto sepiolite. At high concentrations, more lead (II) is left unadsorbed in the solution due to saturation of the binding sites. During the ion exchange process, the $\mathrm{Pb^{2+}}$ not only moved through the pores of the adsorbent mass, but also through the channels of the lattice. Diffusion was faster through pores and was retarded when the ion moved through the smaller diameter channels.

3.3. Effect of contact time

The rate at which adsorption takes place is of the upmost importance when designing batch adsorption experiments. It is important to establish the time dependence of such a system under various experimental conditions. The experiment runs measuring the effect of contact time on the batch adsorption of metal solution containing different initial lead (II) concentration, pH, and adsorbents at 20°C. This result revealed that adsorption of lead (II) is fast that the equilibrium was achieved within 1 h of contact time. Taking into account these results, a contact time of 1 h was chosen for further experiments. When we compared the removal efficiency of the used adsorbents, the sepiolite was found the most effective adsorbent, but we can say that the removal percentage was almost similar for all of them. In the first 50 min the adsorption of lead (II) has shown the increment, and after that, the time did not affect the adsorption capacity.

3.4. Effect of pH

In order to evaluate the influence of pH on the adsorption of lead (II) by various adsorbents, the experiments were carried out at different initial pH values. In similar research, it was reported that the metal hydroxides have been estimated to occur at pH > 6.5 for $\mathrm{Pb(OH)_2}$, and therefore, in the study, the pH range was chosen between 2 and 6 [13,14]. Removal of lead (II) increases with increasing pH value and a maximum value was reached at an equilibrium pH of around 4. The low degree of adsorption at low pH values can be explained by the fact that, at low pH, values the $\mathrm{H^+}$ concentration is high, and therefore protons can complete with the $\mathrm{Pb^{2+}}$ cations for surface sites, since at low pH levels, lead (II) is present in solution as lead (II) free cations.

The lead (II) uptake was found to increase with increasing pH, and it increased rapidly for an increase in pH from 2 to 3. For three solutions of different initial lead (II) concentrations (1, 10, and 100 $\mathrm{mg\,L^{-1}}$), the maximum removal of lead (II) appeared at pH 3.0. The increase in metal removal as pH increases could be explained on the basis of a decrease in competition between hydronium and metal ions for the surface sites and also by a decrease in the positive surface charge on the adsorbent, which resulted in a lower electrostatic repulsion between the surface and the metal ions, and hence the uptake of metal ions increased. A similar theory was proposed by several researchers for metal adsorption using different adsorbents [10,15,16]. In an alkaline medium, lead (II) tends to hydrolyze and precipitate instead of adsorption and adsorbent was deteriorated with an accumulation of metal ions, making true adsorption studies impossible [17].

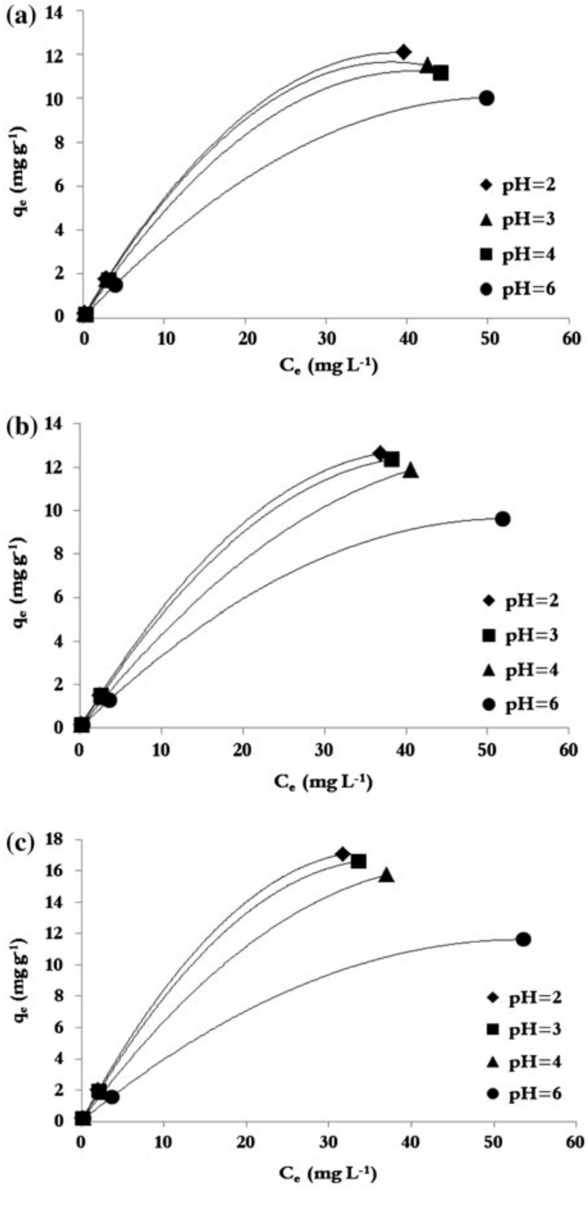

Fig. 1. Adsorption isotherms of Pb^{2+} onto (a) dried activated sludge, (b) diatomite, and (c) sepiolite at different pH ranges.

3.5. Adsorption isotherms

The adsorption isotherm for the removal of metal ions was studied using an initial concentration of 1, 10, and 100 $\mathrm{mg\,L^{-1}}$ at a adsorbent dosage level of 5 $\mathrm{g\,L^{-1}}$ for lead (II). The adsorption equilibrium data are conveniently represented by adsorption isotherms which correspond to the relationship between the mass of the solute adsorbed per unit mass of adsorbent q_e and the solute concentration for the solution at equilibrium C_e (Fig. 1). The Freundlich adsorption isotherm constants, K_F and n, are constants incorporating all factors affecting the adsorption process, such as the adsorption process, the adsorption capacity, and the intensity of adsorption. The constants, K_F and n, were calculated from Eq. (2) using Freundlich plots. The values for the Freundlich constants and correlation coefficients (R^2) for the adsorption process were also presented for all adsorbents in Table 2. The values of n between 1 and 10 (i.e. $1/n$ less than 1) represent favorable adsorption. The values of n, which reflect the intensity of adsorption, also reflected the same trend [18]. From Table 2, it can be seen that experimental data are better fitted to the Freundlich (R^2 = 0.999) than Langmuir (R^2 = 0.972) adsorption isotherm.

The theoretical Langmuir isotherm is plotted together with the experimental data points and the values of the Langmuir constants, a_L, K_L, and $Q_{\max}$, with the correlation coefficient are listed in Table 2 for lead (II). The value of the correlation coefficient is higher than the other two isotherms values. In all cases, the Freundlich equation represents the best fit of experimental data than the other isotherm equations.

As can be seen in Table 2, the Freundlich model fits the data of lead (II) for all adsorbents, as indicated by the values of the coefficient of determination, R^2, of 0,992, 0.997, and 0.997 for lead (II) onto dried activated sludge, diatomite, and sepiolite at pH 3, respectively. The Freundlich isotherm provides the information about the surface heterogeneity and the exponential distribution of the active sites and their energies; it does not predict any saturation of the surface of the adsorbent by the adsorbate. Hence, infinite surface coverage could be predicted mathematically. In contrast, the DKR isotherm relates the heterogeneity of energies close to the adsorbent surface.

A plot of C_{abs} vs. ε^2 gave a straight line from which values of λ and X_m for lead (II) were evaluated and the constants were given in Table 3. From Table 3, it can be seen that the DKR parameters correlation coefficient (R^2) are 0.823, 0.795, and 0.798 for dried activated sludge, diatomite, and sepiolite, respectively.

Table 2
Langmuir and Freundlich parameters for the adsorption of lead (II) by dried activated sludge, diatomite, and sepiolite

	Langmuir				Freundlich		
pH	a_L (L mg^{-1})	K_L (L g^{-1})	$Q_{\max}$ (mg L^{-1})	R^2	K_F (mg g^{-1})	n (L g^{-1})	R^2
	Dried activated sludge						
2	0.039	0.772	19.795	0.9745	0.687	1.260	0.9980
3	0.032	0.639	19.845	0.9998	0.568	1.207	0.9914
4	0.030	0.591	19.440	0.9997	0.534	1.209	0.9931
6	0.022	0.424	19.013	0.9985	0.400	1.185	0.9954
8	0.019	0.269	14.385	0.9766	0.271	1.210	0.9981
	Diatomite						
2	0.028	0.691	24.946	0.9885	0.619	1.174	0.9977
3	0.025	0.631	25.24	0.996	0.571	1.161	0.9971
4	0.020	0.531	26.158	0.972	0.498	1.155	0.9990
6	0.021	0.386	18.558	0.9997	0.362	1.174	0.9951
8	0.013	0.241	18.538	0.9287	0.244	1.161	0.9998
	Sepiolite						
2	0.032	1.079	33.93	0.9908	0.944	1.171	0.9975
3	0.029	0.981	33.37	0.9968	0.865	1.163	0.9968
4	0.024	0.803	33.18	0.9793	0.733	1.161	0.9986
6	0.026	0.517	19.88	0.9812	0.487	1.233	0.9976
8	0.010	0.313	30.38	0.9957	0.308	1.108	0.9986

The free energy, E, is between 0.79 and 1.73 kJ mol^{-1}, which is obtained using Eq. (4). Since E values found in this work are less than 2 kJ mol^{-1}, the type of adsorption is physical adsorption due to weak Van der Waals forces.

Table 3
DKR parameters for the adsorption of lead (II) by dried activated sludge, diatomite, and sepiolite

pH	X_m (mg g^{-1})	β ($\times 10^{-8}$ mol^2 J^{-2})	E (kJ mol^{-1})	R^2
	Dried activated sludge			
2	4.935	−0.187	1.64	0.8060
3	4.856	−0.249	1.42	0.8230
4	4.682	−0.258	1.39	0.8193
6	4.136	−0.322	1.25	0.8136
8	3.167	−0.400	1.12	0.8017
	Diatomite			
2	4.756	−0.195	1.60	0.7935
3	4.672	−0.213	1.53	0.7957
4	4.388	−0.232	1.47	0.7863
6	3.766	−0.305	1.28	0.8022
8	3.005	−0.381	1.15	0.7779
	Sepiolite			
2	6.434	−0.168	1.73	0.7960
3	6.292	−0.183	1.65	0.7980
4	5.853	−0.204	0.79	0.7897
6	4.537	−0.262	0.79	0.7945
8	4.108	−0.411	0.79	0.7882

3.6. Adsorption kinetics

A linear form of the pseudo-first-order model was described by Lagergren according to Eq. (8). A linear plot $\log(q_e - q_t)$ vs. time allows one to obtain the rate constant (Fig. 2). If the plot is found to be linear with a good correlation coefficient, then this indicates that the Lagergren's equation is appropriate for lead (II) adsorption on adsorbent. So, the adsorption process is a pseudo-first-order process. The Lagergren's first-order rate constant (k_1) and q_e determined from the model are presented in Table 4 along with their corresponding correlation coefficients. It was observed that the pseudo-first-order model did not fit well. This suggests that the adsorption of lead (II) does not follow first-order kinetics. The lead (II) adsorption curve fitted the Lagergren first-order model only for dried activated sludge, and R^2 values of 0.92, 0.96, and 0.97 were observed for 1, 10, and 100 mg L^{-1} lead (II), respectively.

The pseudo-second-order model is based on the assumption that chemisorption of the sorbate will take place. The kinetic model can be represented as Eq. (8)

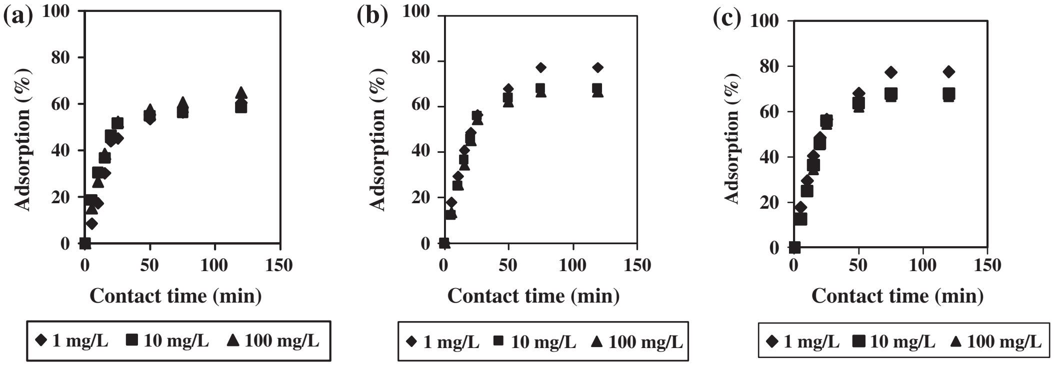

Fig. 2. Lagergren for dried (a) activated sludge, (b) diatomite, and (c) sepiolite.

Table 4
Lagergren first-order rate constants for dried activated sludge, diatomite, and sepiolite

Pb^{2+} concentration ($mg\ L^{-1}$)	$k_{1,ads}$ ($\times 10^{-3}\ min^{-1}$)	R^2
Dried activated carbon		
1	27	0.9237
10	27	0.9564
100	39	0.9714
Diatomite		
1	25	0.8441
10	26	0.500
100	33	0.1520
Sepiolite		
1	14	0.8241
10	25	0.9423
100	28	0.9327

Table 5
Pseudo-second-order kinetic parameters for dried activated sludge, diatomite, and sepiolite

Pb^{2+} concentration ($mg\ L^{-1}$)	q_e ($mg\ g^{-1}$)	k_2 ($g\ mg^{-1}\ min^{-1}$)	R^2
Dried activated sludge			
1	1.358	0.038	0.9886
10	12.18	0.011	0.9989
100	138.9	5.8×0^{-4}	0.8404
Diatomite			
1	158.7	4.07×10^{-4}	0.9921
10	144.9	3.5×10^{-4}	0.9873
100	135.0	4.7×10^{-4}	0.9968
Sepiolite			
1	166.7	4.3×10^{-4}	0.9974
10	147.0	5.07×10^{-4}	0.9927
100	143.0	5.4×10^{-4}	0.9947

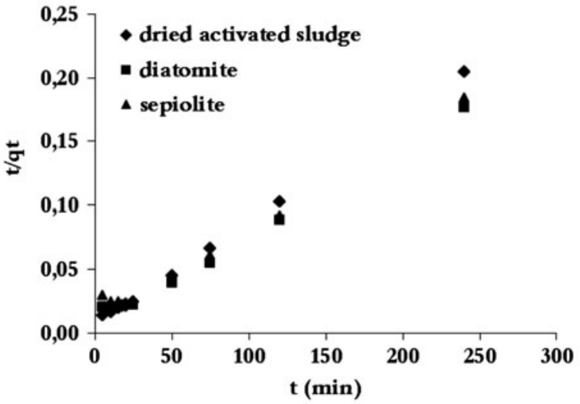

Fig. 3. Pseudo-second-order kinetics plots for the adsorption of Pb^{2+} onto dried activated sludge, diatomite, and sepiolite.

and the constants (k_2 and q_e) can be experimentally determined from the plot (t/q_t) against t as shown in Fig. 3. In the beginning of the experiments, the samples were taken at the interval of five minutes due to the high adsorption rate achieved in the first 30 min. For the removal of lead (II), the pseudo-second-order

Table 6
The levels of variables chosen for the trials

pH	Initial concentration, C_{in} ($mg\ L^{-1}$)	Type of adsorbent, *S*
2 (−1)	1 (−1)	Dried activated sludge (−1)
3 (0)	10 (0)	Diatomite (0)
6 (1)	100 (1)	Sepiolite (1)

model fits the experimental data very well. The R^2 values for lead (II) removal are 0.989, 0.992, and 0.997 for dried activated sludge, diatomite, and sepiolite, respectively. The adsorption of lead (II) on dried activated sludge, diatomite, and sepiolite can thus be considered following the pseudo-second-order kinetics. For lead (II) removal, in this study, an R^2 value of 0.84 for all lead (II) concentrations is also better than that for the first-order kinetics. Therefore, it can be concluded that the second-order kinetics model better describes the adsorption of lead (II) for all adsorbents studied in this paper (Table 5).

3.7. Experimental design

The results of the experimental design were studied and interpreted by DOE++ statistical software to estimate the response of dependent variable. A Box–Behnken design of three factors at three levels was chosen. pH (*A*), initial concentration (*B*), and type of adsorbent (*C*) were selected as independent factors, and the removal efficiency of lead (II) adsorption (%) was chosen to be the response of the system as a dependent variable. In a system involving three significant independent variables, *A*, *B*, and *C*, the mathematical relationship of the response on these variables can be approximately calculated by the quadratic polynomial equation:

$$RE = 70 - 11.61A - 7.65B + 3.64C - 0.35AB - 0.43AC - 6.89A^2 - 3.21B^2 - 0.19C^2 \tag{9}$$

The low, middle, and high levels of each variable were designated as −1, 0, and 1, respectively. These values are given in Table 6. Computation was carried out using multiple regression analysis using the least squares method. Fig. 4 shows the mean of the experimental results for the respective low, medium, and high levels of pH, initial concentration, and type of adsorbent. Analysis of variance (ANOVA) tests the significance and the adequacy of the regression model [19–21]. ANOVA subdivides the total variation of the results into two components: variation associated with the model and variation associated the experimental error, showing whether the variation form the model is significant or not when compared with the ones associated with residual error. The summary of the ANOVA is shown in Table 7. The regression coefficient (R^2) quantitatively evaluates the correlation between the experimental data and the predicted responses. The obtained R^2 values suggest good adjustments to the experimental results since these indicate that 99.72% of the variability in the response could be explained by the models.

Prob > *F* is the probability that all the variations in the results are due to random error, and thus the very low values obtained for lead (II) indicate that results are not random, and the terms in the models have a

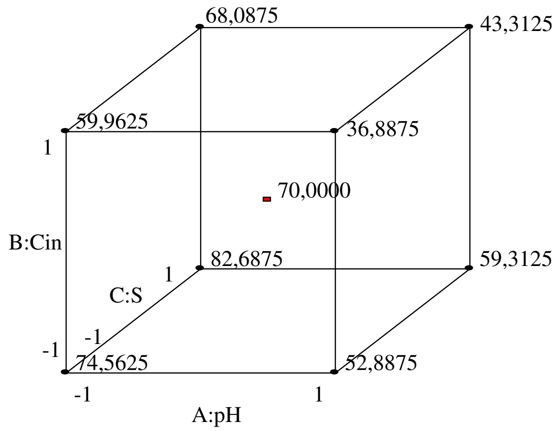

Fig. 4. Cube plot for Pb^{2+} removal efficiency.

Table 7
ANOVA, regression coefficient estimate, and test of significance for lead (II) removal (response surface quadratic model)

Source of variation	Degrees of freedom	Sum of squares (partial)	Mean squares (partial)	*F* ratio	*P* value
Model	9	1932.2536	214.6448	317.9193	3.01E−09
Linear effects	3	1652.8325	550.9442	815.8359	2.77E−10
Interaction effects	3	1.2125	0.4042	0.5985	0.6337
Quadratic effects	3	278.2086	92.7362	137.3234	3.22E−07
Residual	8	5.4025	0.6753	–	–
Lack of fit	3	5.4025	1.8008		
Pure error	5	0	0		
Total	17	1937.6561			

R^2 = 99.72%, R^2 (adj) = 99.41%, R^2 (pred) = 95.54%.

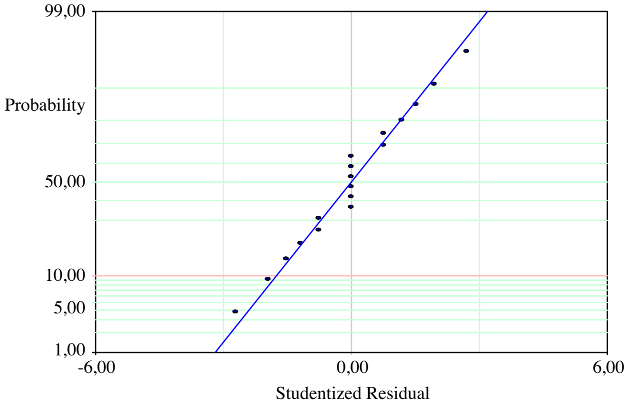

Fig. 5. Normal % probability vs. residual error.

significant effect in the response. Data were also analyzed to check the normality of the residuals. A normal probability plot of these residuals is shown in Fig. 5.

The data points on this plot are reasonably close to a straight line, lending support to the conclusion that pH, C_{in}, S, pH^2, C_{in}^2, and S^2 are the significant factors and that the underlying assumptions of the analysis are satisfied. Contour and surface plots in Fig. 6 were plotted to understand both the main and interaction effects of the factors. These plots can be obtained by computations using developed response models and software, namely DOE++.

These figures clearly show that the removal of lead (II) decreased with an increase in pH and initial

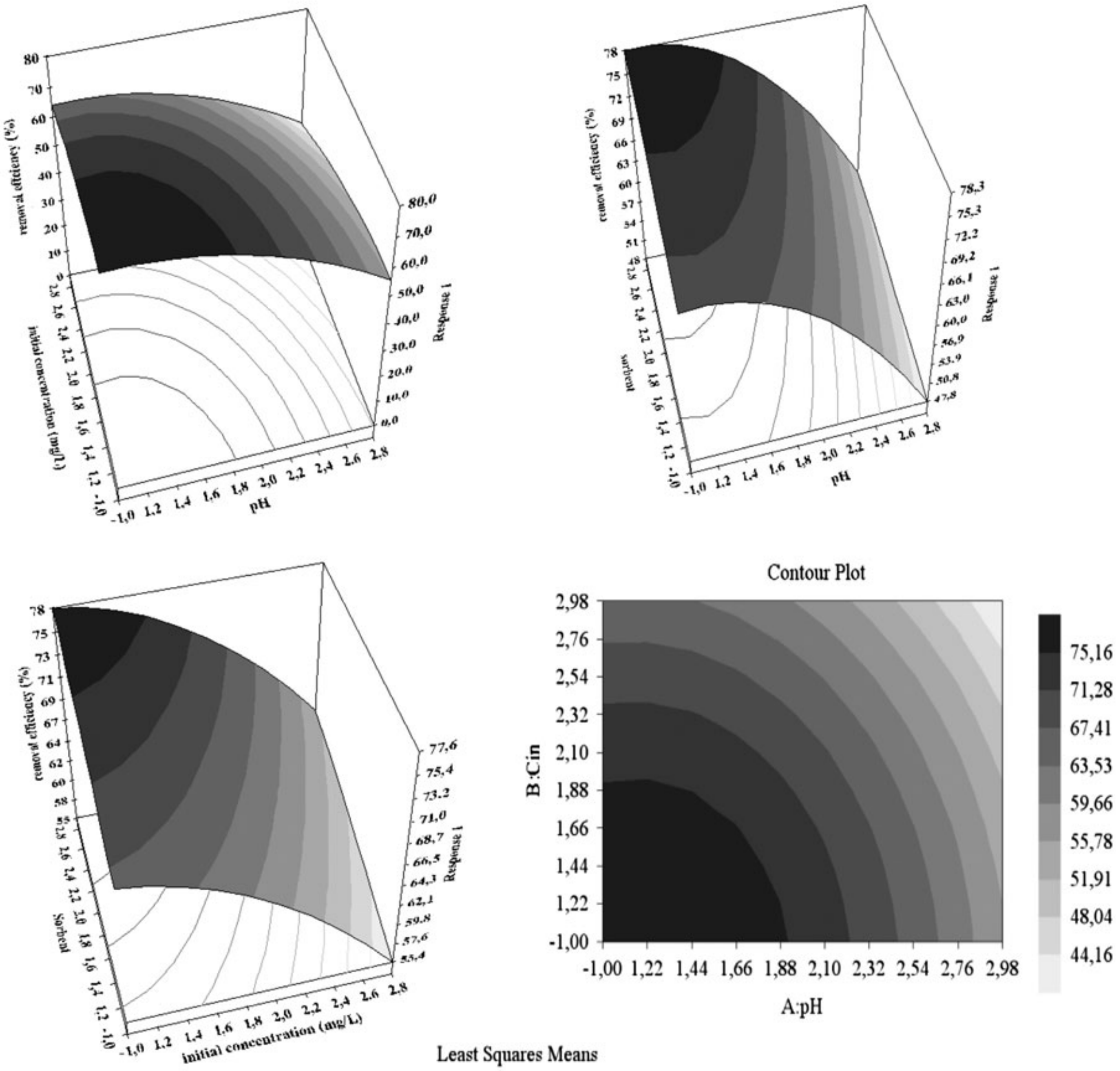

Fig. 6. Surface plots and contour of the estimated response surface of removal efficiencies.

concentration. The surface and contour plots of response (RE) indicated the same results and reveal that the effect of *A* was more significant with lower level of *B*, the effect of *B* was more important with lower level of *B*, but *A* and *B* were more significant with higher level of *C* as sepiolite. From this plot, maximum removal efficiency required lower pH and initial lead (II) concentrations using sepiolite in agreement with the adsorption studies.

4. Conclusions

In this work, the ability of various adsorbents to remove lead (II) from aqueous solution was investigated. Experimental results show that sepiolite was more effective for the removal of lead (II) from aqueous solution than dried activated sludge and diatomite. Since the adsorbents used in this study are freely, abundantly, and locally available, adsorbents, like sepiolite, are expected to be economically viable for the removal of heavy metals from aqueous solutions. The results obtained in this study were modeled using three isotherm models: Langmuir, Freundlich, and DKR. Equilibrium isotherms were best described by the Freundlich equation. The adsorption kinetics can be best described by the pseudo-second-order model equation. The statistical design of the experiments combined with techniques of regression was applied in optimizing the conditions of maximum adsorption of lead (II). The pH of the solution exerted the greatest influence on the removal efficiency.

In conclusion, the application of the response surface method to the adsorption of lead (II) has given an empirical correlation for the adsorption of metal, while it was found that an optimum combination of significant parameters to obtain high coefficients was not discernible; it has highlighted the significance of the pH, initial concentration, and type of adsorbent, which appears to be a critical parameter. Sepiolite was the most suitable adsorbent for the removal of lead (II) from aqueous solutions.

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